

NISTIR 6242

ANNUAL CONFERENCE ON FIRE RESEARCH
Book of Abstracts
November 2-5, 1998

Kellie Ann Beall, Editor

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CROSS-LINKING OF POLYSTYRENE BY FRIEDEL-CRAFTS CHEMISTRY OFFERS ENHANCED THERMAL PROTECTION

Charles A. Wilkie and Michael A. McKinney

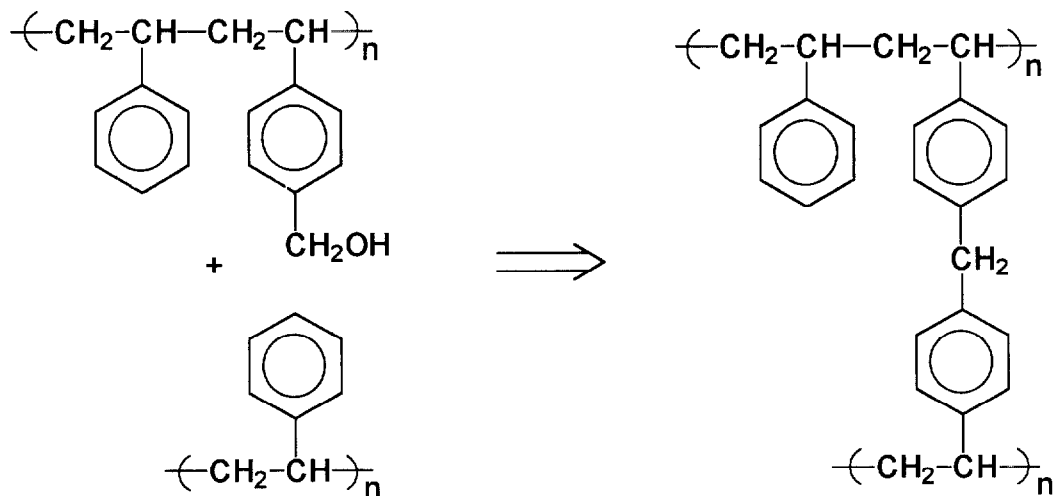
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Work from this laboratory has been focused on developing processes by which one may cross-link polystyrene, under fire conditions, in order to have enhanced thermal properties for this polymer. Friedel-Crafts chemistry is utilized in order to achieve cross-linking. The normal Friedel-Crafts reaction proceeds at room temperature and uses an alkyl chloride as the alkylating agent and aluminum chloride as the catalyst.



This reaction is clearly unsuitable due to the evolution of hydrogen chloride and the presence of aluminum chloride as catalyst. An alcohol can also be used as the alkylating agent and materials such as zeolites may be effective catalysts for the reaction.

The system with which we have had the most success is a copolymer of styrene and *p*-vinylbenzyl alcohol. We have used a copolymer which contains at most 10% of the alcohol component and in many cases we have reduced the amount to a few per cent of alcohol. Below is shown a schematic of the cross-linking reaction.



This copolymer undergoes spontaneous cross-linking at 200°C when the percentage of alcohol is about 15% but there is no cross-linking, in the absence of a catalyst, when the alcohol content is reduced to 5% or less. Somewhat traditional Friedel-Crafts catalysts, Lewis acids such as CuCl_2 , CoCl_2 , ZnCl_2 , MnCl_2 ,

SnCl_2 , and NiCl_2 , effect the cross-linking reaction when the copolymer is heated with 1 to 3% of the catalyst at 250°C for 2 hours. When an intimate blend of the copolymer and additive is subjected to thermogravimetric analysis, the temperature at which 10% degradation occurs is increased by 40 to 90°C , depending on the catalyst, and the amount of residue which is non-volatile increases from 4 to 8%, depending on the catalyst. Of more interest is the fact that zeolites and phosphate esters will also catalyze the reaction. The phosphate ester, 2-ethylhexyl-diphenylphosphate, is of particular interest. Bronsted acids are also known to catalyze Friedel-Crafts chemistry and this phosphate ester is a protected substituted phosphoric acid. When 2-ethylhexyl-diphenylphosphate is heated to 250°C , it eliminates 2-ethylhexene with the formation of diphenylphosphoric acid. Thus one may control the temperature at which reaction occurs, since no reaction will occur until the catalyst has been formed by the thermal decomposition of the ester. The degradation of the copolymer begins 100°C higher in the presence of the phosphate ester than in its absence.

Cone calorimetry of polystyrene, the copolymer, blends of both of these with the phosphate ester have been studied and the results are shown below. It is clear that the rate of heat release is significantly decreased for the blend of the copolymer with the ester and that the presence of the ester has no effect on polystyrene.

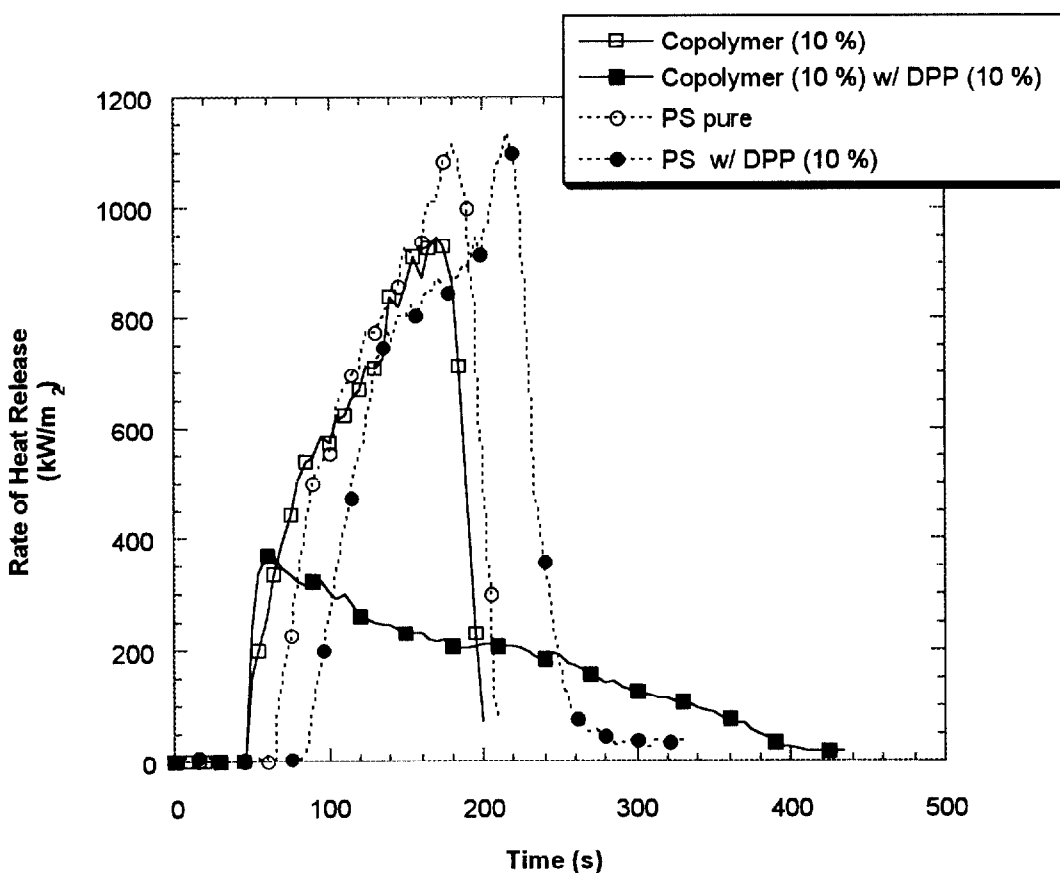


Figure 1. Cone calorimetry of polystyrene, the copolymer, and blends with the phosphate ester.